Thermal diffusivity of ultra thin film of poly-imide by temperature wave analysis

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1. INTRODUCTION

Thermal conduction is an important factor strongly influences the performance of micro-machined devices or the integrated circuits that require effective removal of increasing heat fluxes from the active regions. The simulation of these devices requires thermal property data for the thin-film materials from which they are made. The thermal conductivity and thermal diffusivity of polymers are of particular importance because they govern the temperature-rise magnitude and the temporal thermal behaviour of polymer-based products in silicon-based microelectronics industry.

Thermal diffusivity of ultra thin polymer film has been measured by a temperature wave method (TWA) developed in our laboratory [1-3]. In the case of poly-imide of 0.12μm thick, it is possible to observe the temperature wave diffusion up to 100kHz in frequency.

The features of this temperature wave technique are as follows.

(i) A thin sputtered metal layer with a small area size is used as a temperature sensor. The heat capacity of the sensor is negligible and it is sensitive to the small temperature variation up to 100kHz. The good thermal contact is also attained for a high accuracy.

(ii) The sensor position (on which a temperature wave is detected) is located a distance d from a heater position (on which a temperature wave is generated.). It is more sensitive to detect a small change in the molecular anisotropy of materials in the forced state or in the complicated phase transition.

(iii) By inputting harmonics of the temperature wave (such as a square wave or a triangle wave or a multiple sinusoidal wave) the simultaneous measurement of thermal diffusivity at multiple frequencies is possible, named as Fourier transform

temperature wave analysis (FT-TWA[10]).

(iv) If once a reference material is introduced for the calibration of amplitude of the temperature wave, heat capacity per unit volume [2),10)] and thermal conductivity can be determined..

This manuscript discusses the applicability of TWA for the measurement of ultra thin film of poly-imide with a thickness less than 1μm. The relationship between the processing condition (the rotation speed, viscosity, temperature) and thermal diffusivity will be precisely examined.

2. EXPERIMENTAL

Ultra thin polyimide films were prepared by the spin-coating method. The flat glass plate of Pyrex 7740 with the thickness of 2mm, on which the thin gold layers were sputtered in an area size of 1mm x 4mm, was used as a base plate in the spin-coating. An electric resistance of the gold layer was controlled at 50 Ω that is used as a thermal sensor. The varnish of polyimide (BPDA-PPDA[4], Hitachi Chemicals, Co. Ltd.) was spin-coated on the glass plate under a control of the rotating speed, 500~3000rpm. The thickness was controlled both by the rotating speed and the viscosity of the varnish. After the spin-coating the specimens were dried in the nitrogen atmosphere at 140^{o}C, 200^{o}C, and 350^{o}C with 60 min each. Fig.1 shows the relationship between the thickness of the spin-coated film, the rotating speed of spin-coater, and the viscosity of the varnish, (1)1500mPa・s, (2)130mPa・s, (3)60mPa・s, and (4) 8mPa・s. After the annealing process a gold thin layer for generating a temperature wave is sputtered on the spin-coated film opposite side to the sensor on the glass plate.

Figure 2 shows a schematic diagram of the measuring system. The instrument consists

of a specimen holder with a hot stage, a function synthesizer (NF1942) inputting a.c. current on a heater, a two-phase digital lock-in amplifier (SR830), temperature control system, and a D.C. source for a bias current for a temperature signal.

A temperature wave is put into the specimen by a.c. Joule heating with variable frequency and the heat power on a heater is adjusted less than 100mW. The generated temperature wave propagates in the thickness direction to the rear surface. The temperature variation on the rear surface is detected by the resistance variation of a resistor. Lock-in amplifier detects the phase delay between the heater and the sensor and the amplitude decay is also recorded as a function of frequency at a locked frequency. The lock-in technique is advantageous to get the phase component of temperature wave without any influences from the DC temperature variation from the sensor or heat loss.

3. COMPUTATIONAL PROCEDURE

Assuming the one-dimensional heat flux, the temperature wave generated on the front surface ($x=0$) by a.c. Joule heating propagates in the thickness direction and is detected by the sensor attached on the rear surface ($x=d$), on which the amplitude decay and the phase delay can be observed. The one-dimensional diffusion equation leads to the solution of temperature oscillation at $x=d$ as follows;

$$T(d,t) = \frac{\left\{ j_0 exp\left(i\,\omega\, t\right) / \left(1+i\right) \right\} exp\left\{ -\left(1+i\right) kd \right\}}{\left[\left(\lambda k + \lambda_s k_s\right)^2 - \left(\lambda k - \lambda_s k_s\right)^2 exp\left\{ -2(1+i)kd \right\} \right] / 2\lambda k} \qquad (1), \qquad k = \sqrt{\frac{\omega}{2\alpha}}$$

,

where T is a.c. temperature, t is time, j_0 is heat flux on the heater, λ is thermal

conductivity, α is thermal diffusivity and ω is angular frequency. Subscript *s* means the property of backing substrates and the other means the specimen. If the conditions of (i) $kd>>1$ or (ii) $\lambda k \sim \lambda_s k_s$ are satisfied, eq.(1) becomes to a simple form of

$$T(d,t) = \frac{\sqrt{2}\, j_0 \lambda k \exp(-kd)}{(\lambda k + \lambda_s k_s)^2} \exp\left\{ i\left(\omega t - kd - \frac{\pi}{4}\right)\right\} \qquad (2)$$

.

To note the phase term in eq.(2), we can get more simple equation as follows.

$$\Delta\theta = -\sqrt{\frac{\omega}{2\alpha}}\, d - \frac{\pi}{4} \qquad (3)$$

When the thickness *d* has been already known, the thermal diffusivity is calculated from the slope of the linear relationship between $\Delta\theta$ and $\omega^{1/2}$ in eq. (3). In eq.(2) thermal diffusivity is also calculated from the amplitude decay, that includes the information of thermal diffusivity and heat capacity, however, it needs the correction by the reference material to evaluate the input thermal energy or heat losses with high accuracy. On the other hand the phase component is an absolute value as a function of thickness, thermal diffusivity, and angular frequency, without any reference materials. In this study the phase component of temperature wave, that is independent of the instrument constant or the absolute value of the thin metal resistor, is used for the calculation of thermal diffusivity of ultra thin films.

4. RESULTS AND DISCUSSION

Figure 3 shows the phase shift of spin-coated ultra thin films, prepared in the various conditions, plotted as a function of angular frequency of temperature wave. The curvature of the plot shows a linear relationship in the higher frequency as expected in eq. (3). It is noteworthy that a linear relationship is precisely observed up to 100kHz.

The thickness of the gold sputtered sensor in this study is several ten nanometers by the photographs taken by AFM. The heat capacity of the sensor is negligible enough and it can be applied to detect the thermal signal up to 100kHz under the consideration of thermal diffusion length, although an increase of electric impedance at higher frequency affects the amplitude of the signal. From the curvature of each plot in Fig.3 thermal diffusivity can be calculated. For the calculation of thermal diffusivity, the lower or the higher frequency was excluded, because of an exceptional conditions of eq.(3) or a poor S/N ratio.

The thermal diffusivity calculated from the curvature in Fig.3 is plotted in Fig.4 as a function of the rotating speed of spin-coater. Thermal diffusivity depends on the rotating speed and the viscosity of the varnish, which means that the thermal diffusivity of the spin-coated ultra thin film depends on the processing conditions. Thermal diffusivity increases with the higher rotating speed and the lower viscosity.

Fig.5 is a plot of the relationship of the thermal diffusivity and the thickness of the ultra thin film, in which the thickness dependence is clearly observed, the higher thermal diffusivity with decreasing the thickness, except for the case of low viscosity (4). In the calculation procedure the accuracy or the distribution in the measurement of the thickness strongly affects the calculation result of thermal diffusivity. The experimental errors with a repeated measurement are less than 5% for the thickness.

It is known well that the thermal diffusivity of polymer is strongly affected by the molecular anisotropy[5-9], which is originated in the processing condition. As for the film shaped specimen the molecular anisotropy in a planer surface is often observed and the heat transport property in the thickness direction decreases. The result in Fig.5 shows another possibility for the in-plane molecular anisotropy by the spin-coating method. It

suggests the molecular anisotropy in the transverse direction to the planer surface, it might be caused by a complicated back flow in the spin-coating process with the edge effect of the base glass plate.

In Fig.6 the relationship between the molecular anisotropy observed in the IR spectrum and the thermal diffusivity is shown as a plot of the dichroic ratio at 1500 cm^{-1} by ATR-FTIR and the thermal diffusivity in the thickness direction. The tendency for the increase of the dichroic ratio corresponds to the increase of the molecular anisotropy in the transverse direction to the planer surfaces. The tendency of increasing the thermal diffusivity corresponds roughly to the increase of the dichroic ratio for the different processing conditions. It means that the temperature wave technique is sensitive to detect the small change of thermal diffusivity corresponding to the molecular anisotropy in the ultra thin films with the thickness of sub-micron.

5. CONCLUSION

The applicability of temperature wave analysis to measure the thermal diffusivity of the ultra thin polyimide film was examined. The measurement in high frequency, up to 100kHz, is needed for the appropriate thermal condition for the sub-micron films. It is shown that the temperature sensor of sputtered thin metal layer is sensitive enough to detect the phase shift of temperature wave at high frequency. In addition the thermal diffusivity of spin-coated polyimide film increases with the decrease of the thickness in the processing condition in this study, that has a good coincidence with the tendency of molecular anisotropy observed by ATR-FTIR.

REFERENCES

1. J Morikawa, and T Hashimoto Jpn. J. Appl. Phys. Vol. 37 (1998) pp. L1484-L1487.
2. J.Morikawa, T.Hashimoto, A.Maesono, High Temp.-High Press., vol.33 p387 (2001).
3. J.Morikawa, Junji Tan and Toshimasa Hashimoto, Polymer, **36**, 4439 (1995).
4. D. Boese, S. Herminghaus, D.Y. Yoon, J.D.Swalen, and J.F. Rabolt, Mat. Res. Soc. Symp.Proc. Vol.227 (1991) 379.
5. T. P. Russell, H. Gugger, J. Swalen, J. Polym. Sci., Polym. Phys. Ed., 21 (1983) 1745.
6. L. Lin, S.A.Bidstrup, J. Appl. Polym. Sci., 49 (1993) 1277.
7. M. Ree, C. W. Chu, M. J. Goldberg, J. Appl. Phys., 75, (1994) 1440.
8. F. Li, K. H. Kim, E. P. Savitski, J.C.Chen, F.W. Harris, S.Z.D.Cheng, Polymer, 38 (1997) 3223.
9. S. Matsuda, S. Ando, J. Polym Sci, B Polum. Phys.,41 (2003) 418.

FIGURE CAPTIONS

Fig.1 The relationship between the rotation speed of spin coater and the thickness of the spin-coated polyimide films on the glass plate with various viscosity. (1) 1500mPas, (2) 130mPas, (3) 60mPas, (4) 8mPas.

Fig.2a Schematic diagram of measurement sysytem.

Fig.2b An example of the measurement cell with a spin-coated specimen.

Fig.3 Phase delay Dq plotted as a function of square root of angular frequency of temperature wave in the thickness direction of spin-coated polyimide film.

Fig.4 The relationship between the thermal diffusivity and the rotation speed with various viscosity.

Fig.5 Thermal diffusivity plotted against the thickness of spin-coated polyimide films.

Fig.6 The relationship between the molecular anisotropy determined by IR spectrum and the thermal diffusivity.

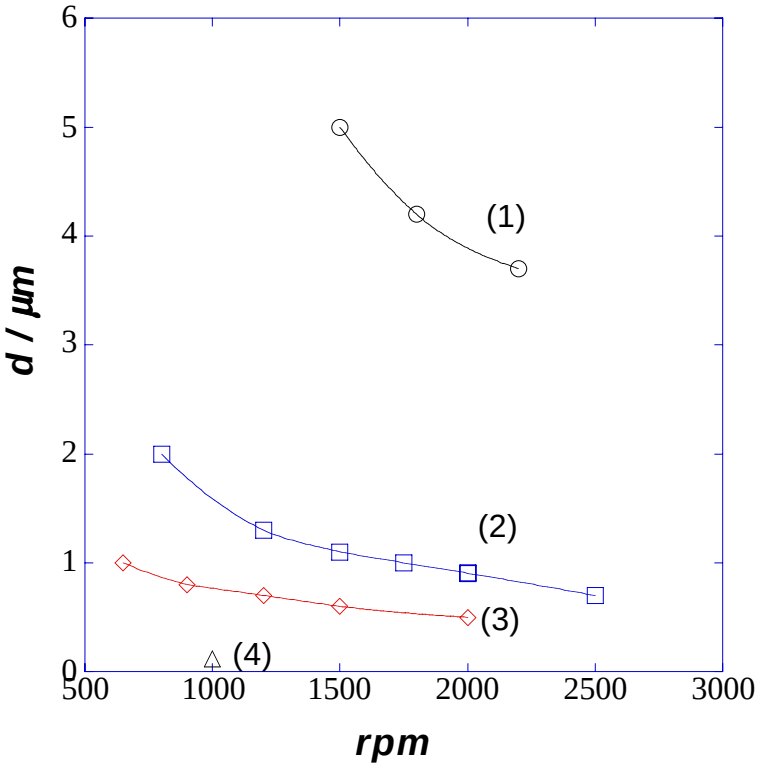

Fig.1 The relationship between the rotation rate of the spin-coater and the thickness of polyimide coated on the glass plate. The viscosity of the varnish is (1)1500mPa・s, (2)130mPa・s, (3)60mPa・s, and (4)8mPa・s.

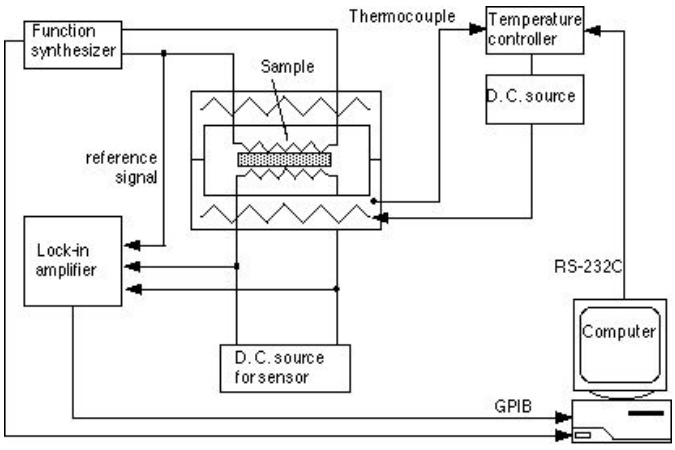

Fig.2a Schematic diagram of the measurement apparatus.

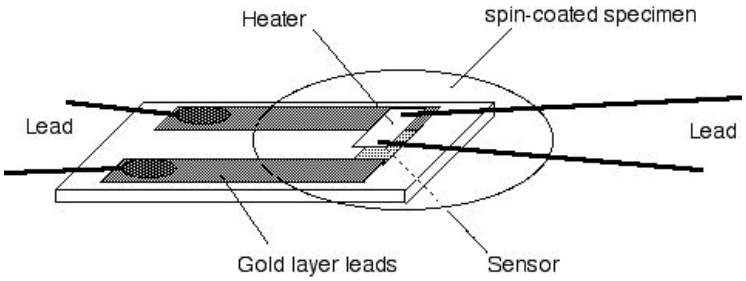

Fig.2b An example of measurement cell with a spin-coated specimen.

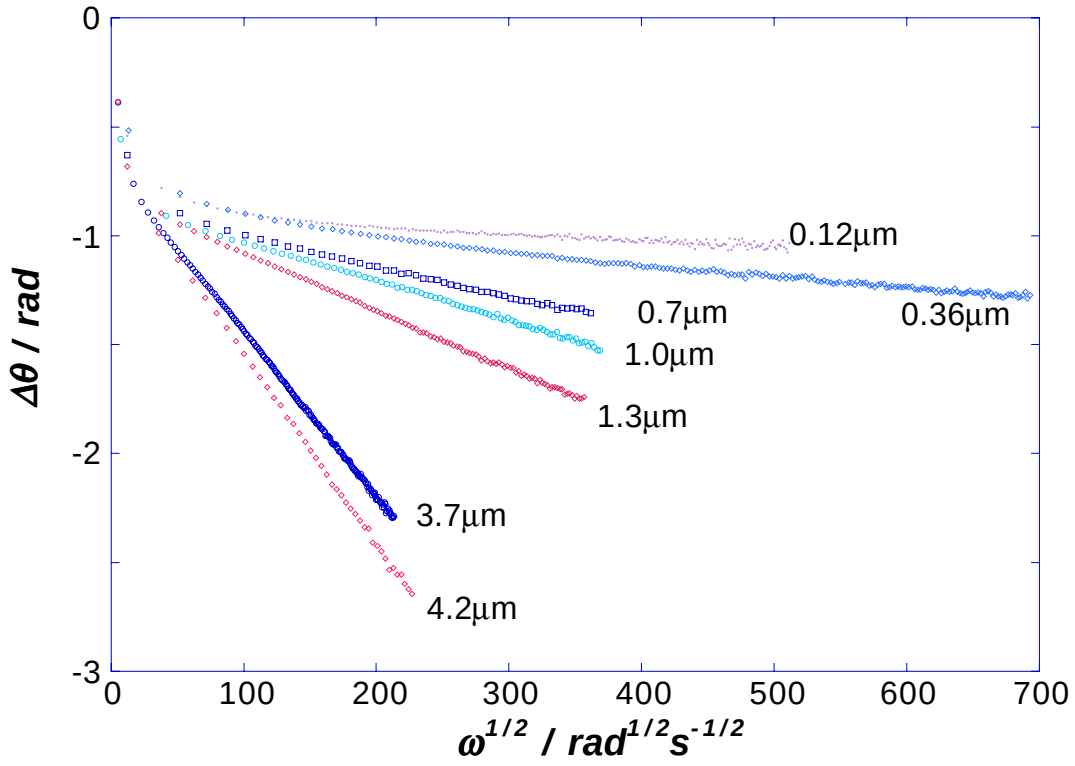

Fig.3 Phase delay Dq plotted as a function of square root of angular frequency of temperature wave propagating in the thickness direction in the spin-coated polyimide film.

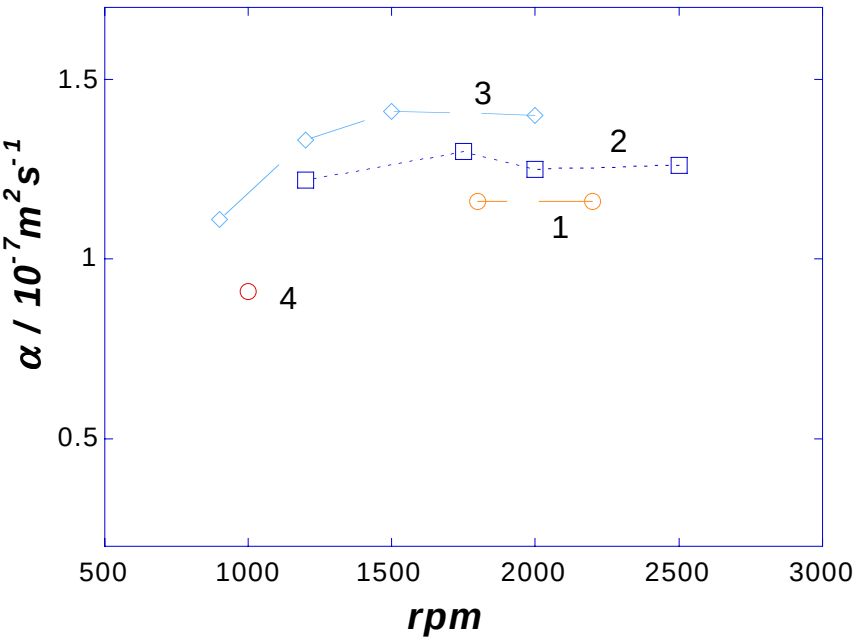

Fig.4 The relationship between the thermal diffusivity of the spin-coated polyimide and the rotation speed in a spin-coating with various viscosity of varnish, (1)1500mPa・s, (2)130mPa・s, (3)60mPa・s, and (4) 8mPa・s.

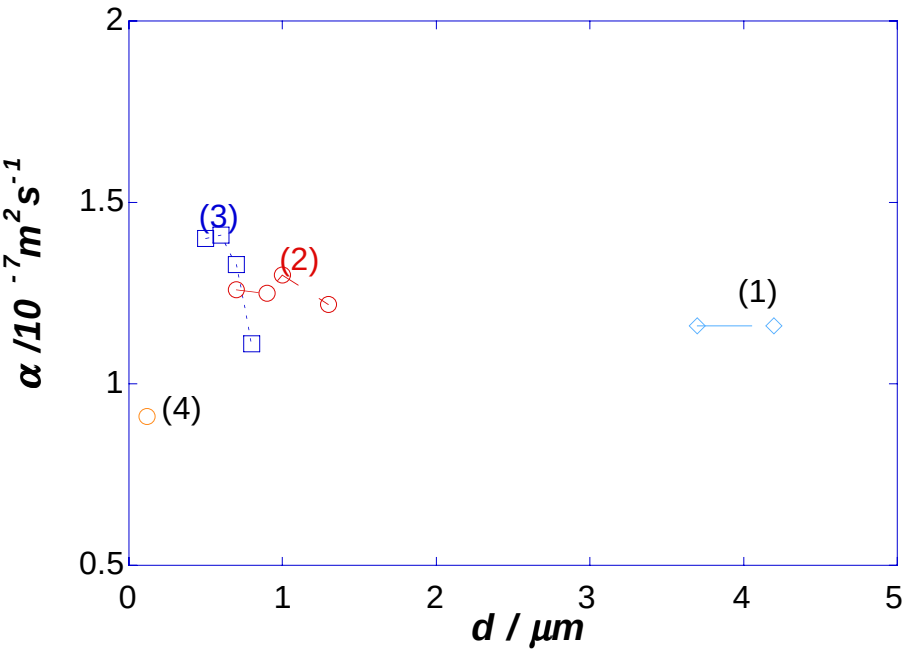

Fig.5 The relationship between the thermal diffusivity and the thickness of spin-coated polyimide with various viscosity of varnish.

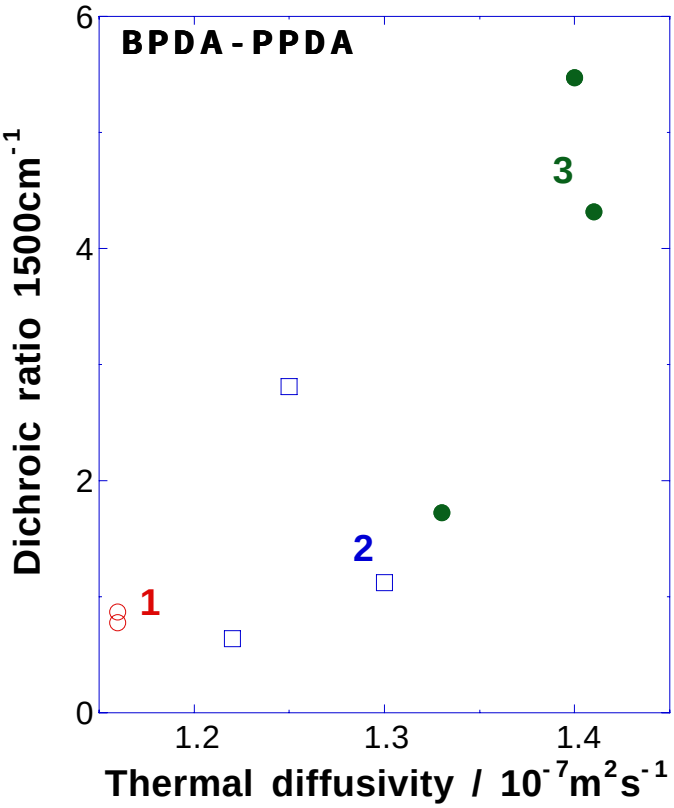

Fig.6 The relationship between the molecular anisotropy determined by IR spectrum and the thermal diffusivity.